

Materials Chemistry

Cite this: *J. Mater. Chem.*, 2012, **22**, 10650www.rsc.org/materials

PAPER

Novel N[^]C[^]N-cyclometallated platinum complexes with acetylide co-ligands as efficient phosphors for OLEDs†

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Received 14th December 2011, Accepted 17th March 2012

DOI: 10.1039/c2jm16592a

Two new cyclometallated platinum(II) complexes have been prepared that incorporate a terdentate N[^]C[^]N-coordinating ligand and a monodentate acetylide co-ligand. The complexes, namely [PtL³–C≡C–C₆H₃F₂] and [PtL⁶–C≡C–C₆H₃F₂] (where HL³ = 5-methyl-1,3-di(2-pyridyl)benzene; HL⁶ = 5-mesityl-1,3-di(2-pyridyl)benzene; H–C≡C–C₆H₃F₂ = 3,5-difluorophenylacetylene), were prepared by ligand metathesis from the corresponding chloro complex PtLⁿCl. Both of the new complexes are intensely luminescent in solution, displaying quantum yields superior to PtLⁿCl. OLEDs have been prepared using the new compounds as phosphorescent emitters. Although both lead to efficient devices, the best electroluminescence quantum efficiencies are obtained with the derivative of HL⁶, having the mesityl group on the cyclometallated phenyl ring. The superior performance with this complex can be rationalised in terms of the greater steric hindrance that serves to reduce aggregate-induced quenching.

Introduction

Organometallic complexes that emit efficiently from triplet excited states are of great interest due to the numerous applications of such compounds. For example, the new generation of display screen technology – organic light-emitting devices (OLEDs) – can benefit from the incorporation of such materials to promote emission from otherwise wasted triplet states.^{1–4} Meanwhile, triplet excited states of coordination and organometallic complexes may be sufficiently long-lived for other processes to occur following absorption of light, such as energy and electron transfer, central to the field of light-to-chemical energy conversion.⁵

In OLEDs, light emission arises from the radiative deactivation of electronically excited states that are formed by recombination of charge carriers, *i.e.* electrons and holes, injected from the electrodes. Because phosphorescent emitters doped into fluorescent host materials can potentially harvest both singlet and triplet excitons upon electron–hole recombination,

their use instead of fluorescent compounds may potentially improve the luminous efficiency by a factor of up to four. Complexes of third-row transition metal ions are particularly appropriate for this purpose, since the high spin-orbit coupling constant associated with them efficiently promotes triplet radiative decay.^{2,6}

Although iridium(III) complexes are predominant in this field, increasing attention is focused on platinum(II) complexes, particularly due to their propensity to undergo face-to-face bimolecular interactions leading to excimeric or aggregate emissions.⁷ In the last few years, several families of Pt(II) complexes have been discovered that are brightly luminescent in solution at room temperature, and a number of investigations have shed light on the factors that govern their luminescence efficiencies.⁷ Strong-field ligands or co-ligands tend to favour emission efficiencies, as they raise the energies of otherwise deactivating d–d states, making them thermally inaccessible and thus reducing non-radiative decay pathways.⁷

In particular, the substitution of weak-field halide co-ligands (X) by strong-field cyanides or, even better, by acetylides in complexes of the type Pt(N[^]N)X₂ and [Pt(N[^]N[^]N)X]⁺ has shown how an increase in the ligand field strength of the ancillary ligand promotes luminescence.⁷ Acetylides are more attractive than cyanides, since the latter tend to lead to a drop in the energy of metal-centered orbitals. The beneficial effect of displacing d–d states to high energy is then compromised by a reduced metal character in the excited state, leading to reduced radiative rate constants.⁸ Many interesting, room-temperature luminescent platinum complexes incorporating phosphine,⁹ diimine¹⁰ or terpyridine¹¹ ligands in combination with acetylides have been reported.

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† Dedicated to Dr Hubert Le Bozec, in occasion of his 60th birthday.

A further strategy to improve luminescence is to make use of cyclometallating ligands whose ligand-field strength is augmented, for example, with respect to bipyridine and terpyridine.⁷ Meanwhile, terdentate ligands offer an advantage over bidentate ligands in that the additional rigidity they impart inhibits the D_{2d} distortion that bis-bidentate complexes can undergo through twisting of the two planes relative to one another.¹² Much work has been carried out on cyclometallated Pt(II) complexes with N[^]N[^]C-coordinating ligands such as cyclometallated 6-phenyl-2,2'-bipyridine, whose Pt(II) chloro complex exhibits, in solution at room temperature, an emission quantum yield of 0.025 (ref. 13) increasing to 0.04 upon substitution of the chloride ligand with phenylacetylide, as pioneered by Che and co-workers.¹⁴ The thermal stability and sublimability of Pt(II) acetylide complexes based on cyclometallated 6-phenyl-2,2'-bipyridine render them appropriate for incorporation into the emissive layer of vapour-deposited OLEDs, reaching high luminance and efficiencies (up to 4.2 cd A⁻¹ with a $\eta_{\text{ext}} = 1.6\%$ at 30 mA cm⁻²).¹⁴

Pt(II) complexes with terdentate ligands based on cyclometallated 1,3-di(2-pyridyl)benzene (dpyb),¹⁵ which offer the metal ion an N[^]C[^]N coordination environment with shorter Pt–C bonds than in the isomeric C[^]N[^]N systems, are amongst the brightest Pt-based emitters in solution at room temperature.¹⁶ For example, [Pt(dpyb)Cl] is characterized by an emission quantum yield of 0.60 in deoxygenated dichloromethane.¹⁷ The corresponding complex of the more π -delocalised 1,3-bis-(4'-phenyl-2'-quinoliny)benzene has a lower luminescent efficiency ($\phi = 0.14$), but it can be increased upon substitution of chloride by phenylacetylide ($\phi = 0.21$).¹⁸ Some Pt(II) acetylide complexes with a cyclometallated N[^]C[^]N ligand have recently been found to be of interest in the preparation of photo-responsive supramolecular organometallic nano-sheets¹⁹ and for their nonlinear properties,²⁰ but their use as OLED emitters has not previously been investigated.

In this paper, we present a study of the effect of substitution of the chloride ligand in two [Pt(N[^]C[^]N)Cl] complexes by 3,5-difluorophenylacetylide (–C \equiv C–C₆H₃F₂), and we show how this class of material can be used to prepare efficient OLEDs.

Experimental

General comments

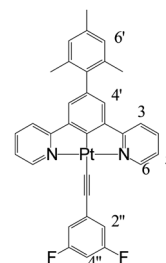
[PtL³Cl] and [PtL⁶Cl] were synthesized as previously reported^{17,21} whereas the new acetylide Pt(II) complexes were prepared as described below. All reagents were purchased from Sigma-Aldrich or Fluorochem and used as received. Products were characterized by infrared and ¹H NMR (Bruker Avance DRX-400 instrument) spectroscopies and by elemental analysis, carried out at the Università degli Studi di Milano.

Synthesis of the new complexes

Complex [PtL³–C \equiv C–C₆H₃F₂]. A mixture of 1-ethynyl-3,5-difluorobenzene (22 mg, 0.16 mmol) and 0.5 M sodium methoxide (2.8 mL, 0.18 mmol) in methanol (1 mL) was stirred for 30 min at room temperature under nitrogen. Then [PtL³Cl] (76 mg, 0.16 mmol) dissolved in a mixture of MeOH (100 mL) and CH₂Cl₂ (25 mL) was added and the mixture was left for one

day with stirring at room temperature. The solution changed colour passing from yellow to red. Then the solvents were removed under reduced pressure and the crude product was washed with water (25 mL), methanol (25 mL), and *n*-hexane (3 \times 25 mL). A further purification by precipitation from dichloromethane/pentane gave the desired product as a red solid in almost quantitative yield (89 mg). ¹H NMR (400 MHz, CDCl₃): δ 9.39 (d, $J(^{195}\text{Pt}) = 50$ Hz, 2H⁶), 7.93 (td, $J_{3,4} = 8.0$; $J_{4,5} = 1.5$ Hz, 2H⁴), 7.66 (d, $J(^{195}\text{Pt}) = 5$ Hz, 2H³), 7.36 (s, 2H^{4'}), 7.21 (td, $J_{5,6} = 5.7$; $J_{4,5} = 1.5$ Hz, 2H⁵), 7.07 (dd, $J_{2'',4''} = 2.3$ Hz; $J(^{19}\text{F}) = 8$ Hz, 2H^{2''}), 6.64 (tt, $J_{4',2''} = 2.3$ Hz; $J(^{19}\text{F}) = 10$ Hz, 1H^{4'}), 2.38 (3H, CH₃). IR $\nu/\text{cm}^{-1} = 2083(\text{C}\equiv\text{C})$. Anal. calcd for C₂₅H₁₆F₂N₂Pt: C, 52.00; H, 2.79; N, 4.85%. Found: C, 52.01; H, 2.83; N, 4.82%.

Complex [PtL⁶–C \equiv C–C₆H₃F₂]. This complex was prepared as described above for [PtL³–C \equiv C–C₆H₃F₂] but starting from [PtL⁶Cl] instead of [PtL³Cl]. ¹H NMR (400 MHz, CD₂Cl₂): δ 9.41 (d, $J(^{195}\text{Pt}) = 40$ Hz, 2H⁶), 8.01 (td, $J_{3,4} = 8.2$; $J_{4,5} = 1.4$ Hz, 2H⁴), 7.70 (d, $J(^{195}\text{Pt}) = 7$ Hz, 2H³), 7.37 (s, 2H^{6'}), 7.31 (td, $J_{6,5} = 5.8$; $J_{4,5} = 1.4$ Hz, 2H⁵), 7.07 (dd, $J_{2'',4''} = 1.0$ Hz; $J(^{19}\text{F}) = 9$ Hz, 2H^{2''}), 7.00 (s, 2H^{4'}), 6.71 (tt, $J_{2'',4''} = 1.0$ Hz; $J(^{19}\text{F}) = 11$ Hz, 1H^{4'}), 2.37 (3H, *p*-CH₃Ph), 2.12 (6H, *o*-CH₃Ph). IR $\nu/\text{cm}^{-1} = 2083(\text{C}\equiv\text{C})$. Anal. calcd for C₃₃H₂₄F₂N₂Pt: C, 58.15; H, 3.55; N, 4.11%. Found: C, 58.20; H, 3.59; N, 3.99%.



Photophysical characterization

Absorption spectra were recorded for dichloromethane solutions using a Biotek Instruments XL spectrometer. Luminescence spectra were recorded using a FluoroMax-2 spectrofluorimeter equipped with an R928 photomultiplier tube. Spectra were corrected for the wavelength dependence of the detector and emission grating. Quantum yields were determined using two independent standards of [Ru(bpy)₃]Cl₂ in H₂O ($\Phi = 0.028$)²² and fluorescein in 0.1 M NaOH solution ($\Phi = 0.90$).²³ The luminescence lifetimes of the complexes were measured by time-correlated single-photon counting, following excitation at 374.0 nm with an EPL-375 pulsed-diode laser. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator.

Electrochemical characterization

Cyclic voltammograms were recorded using an Autolab PG-Stat 30 potentiostat/galvanostat with computer control and data storage via GPES Manager software. Solutions of concentration 1 mM in CH₂Cl₂ were used, containing [Bu₄N][PF₆] 0.1 M as the supporting inert electrolyte. A three-electrode assembly was

employed, consisting of a glassy carbon (GC, 0.071 cm²) or a platinum wire (0.012 cm²) working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The polishing procedure for both working electrodes consisted of surface cleaning with diamond powder (Aldrich, diameter 1 μm) on a wet cloth (DP-Nap, Struers). Since the platinum working electrode showed great fouling effects, the data presented are referred to the glassy carbon working electrode. The voltammetric cell was thermostatted at 298 K and solutions were purged for 5 minutes with solvent-saturated nitrogen gas with stirring, prior to measurements being taken without stirring. The ohmic drop (700–1000 Ω) was duly compensated by the positive feedback technique. The voltammograms were referenced to the ferrocene–ferrocenium couple as the standard ($E_{1/2} = 0.42$ vs. SCE).²⁴ Chemical and electrochemical reversibility was studied using the classical tests.²⁵

Results and discussion

Preparation of the Pt(II) complexes

The cyclometallated N⁴C⁴N Pt(II) chloride precursors [PtL³Cl] and [PtL⁶Cl] were synthesized as previously reported {HL³ = 5-methyl-1,3-di(2-pyridyl)benzene and HL⁶ = 5-mesityl-1,3-di(2-pyridyl)benzene}.^{17,21} Various attempts to substitute the chloride in these complexes by the ethynyl-3,5-difluorobenzene anion following Sonogashira's synthetic route, which has been shown to be suitable for preparing acetylide derivatives of cyclometallated N⁴N⁴C and O⁴N⁴N Pt(II) complexes,^{14,26,27} were unsuccessful, despite the screening of different catalytic systems (for example, CuI–iPr₂NH, CuI–Et₃N, CuOAc–iPr₂NH, and CuOAc–Et₃N). However, [PtL³–C≡C–C₆H₃F₂] and [PtL⁶–C≡C–C₆H₃F₂] were readily obtained in quantitative yield by reaction of PtLⁿCl with the acetylide anion prepared by deprotonation of 3,5-difluorophenylacetylene with sodium methoxide, as shown in Scheme 1.

The new Pt(II) acetylide complexes were fully characterized by elemental analyses and by IR and NMR spectroscopies.

Photophysical and electrochemical properties in solution

Cyclic voltammetry of [PtL³–C≡C–C₆H₃F₂], [PtL⁶–C≡C–C₆H₃F₂] and their chloro analogues was carried out in CH₂Cl₂ solution, and data for the first oxidation and reduction potentials are given in Table 1. All four complexes show a similar reduction peak around –2.3 V. The lack of significant variation with the

co-ligand or central aryl substituent is consistent with the lowest unoccupied molecular orbital (LUMO) being dominated by the pyridyl rings, with little contribution expected from the cyclometallating ring or co-ligand.²⁸ On the other hand, the introduction of the phenylacetylide co-ligand is seen to shift the oxidation potential significantly to less positive potentials for both pairs of complexes, suggesting that the strongly σ-donating acetylide ligand raises the energy of the highest occupied molecular orbital (HOMO). Density functional theory calculations have previously suggested that the HOMO in [Pt(N⁴C⁴N)Cl] complexes is spread over the metal, the co-ligand, and the cyclometallating aryl ring.²⁸ The higher E_{ox} values exhibited by [PtLⁿX] with respect to [PtLⁿX] (X = chloride or acetylide) can thus similarly be explained in terms of the σ-bonding framework in which the mesityl substituent is electron-withdrawing relative to methyl. Steric hindrance between the mesityl and central aryl ring inhibits the attainment of the coplanar conformation that would typically facilitate the counterbalancing π-donation effect in aryl-substituted complexes.²¹

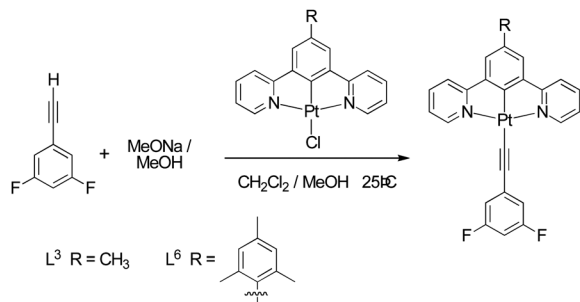
The first oxidation and reduction potentials can be used to estimate the HOMO and LUMO energy levels by means of equations E_{HOMO} (eV) = $-(1.4E_{\text{ox}}) - 4.6$ and E_{LUMO} (eV) = $-(E_{\text{red}} + 4.8)$.^{29,30} The HOMO–LUMO gap is calculated to be 2.57, 3.08, 2.42 and 2.78 eV for [PtL³Cl], [PtL⁶Cl], [PtL³–C≡C–C₆H₃F₂] and [PtL⁶–C≡C–C₆H₃F₂], respectively (Table 1), thus decreasing upon substitution of chloride by 3,5-difluorophenylacetylide.

Absorption and emission data are presented in Table 1. All of the absorption spectra (Fig. 1) show intense bands in the region 260–330 nm, which can be assigned to intraligand ¹π–π* transitions of cyclometallated 1,3-di(2-pyridyl)benzene²¹ and acetylide¹⁸ ligands, and less intense bands at 330–450 nm, corresponding to transitions of mixed charge-transfer/ligand-centred character.²⁸

Although the substitution of the chloride ligand by the phenylacetylide does not change the spectral profile substantially, the individual bands in this region become rather less well-resolved, and there is evidence of a tail to longer wavelength in the phenyl acetylide complexes. This might tentatively be attributed to the introduction of a π_{C≡C} → π*_{N⁴C⁴N} ligand-to-ligand charge-transfer (LLCT) transition, by analogy with other Pt(II) acetylide complexes,^{10,11,18} and as suggested by the observed trend in oxidation potentials discussed above, which indicate that the HOMO is raised in energy upon introduction of the acetylide.

The photoluminescence spectra of the new acetylide complexes, attributed to a primarily ligand-centred ³π–π* state, are quite similar to those of the chloride derivatives (Table 1 and Fig. 2).

They emit brightly in the green region of the spectrum, displaying vibrationally resolved spectra, with the 0–0 band around 510 nm. Like their parent complexes, they readily form excimers at elevated concentration in solution, which emit in the red region of the spectrum around 700 nm (Fig. 2). Complex [PtL³–C≡C–C₆H₃F₂] is a particularly bright emitter, with a luminescence quantum yield of 0.77 in deoxygenated dichloromethane, somewhat superior to the parent chloro complex, and with a similar trend being observed for the complexes of L⁶ (Table 1). Notably, the self-quenching constants of the derivatives of the mesityl ligand L⁶ are significantly lower

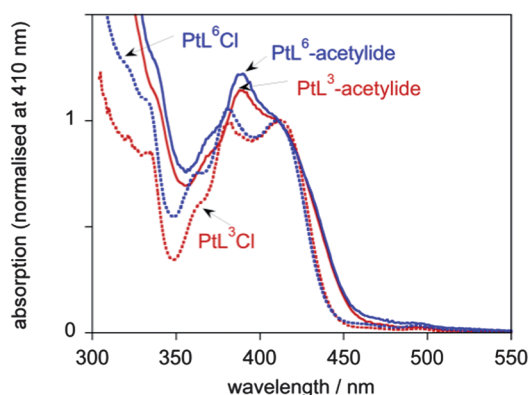
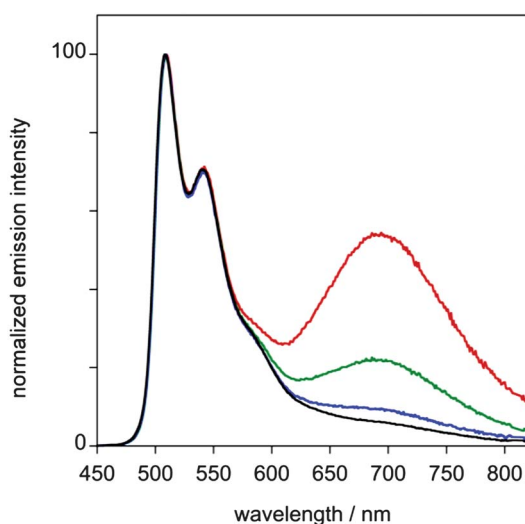


Scheme 1 Synthesis of [PtL³–C≡C–C₆H₃F₂] (R = methyl) and [PtL⁶–C≡C–C₆H₃F₂] (R = mesityl).

Table 1 Photophysical and electrochemical data of the Pt(II) complexes in CH₂Cl₂ at 298 K

	Absorption $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)	Emission $\lambda_{\text{max}}/\text{nm}$	Φ_{lum}^a	$\tau_0^b/\mu\text{s}$	$k_Q^{\text{SQ}b}/10^9 \text{M}^{-1} \text{s}^{-1}$	$k_Q^{\text{O}_2^c}/10^8 \text{M}^{-1} \text{s}^{-1}$	$E_p^{\text{red}d}/\text{V}$	$E_p^{\text{ox}d}/\text{V}$	HOMO ^e /eV	LUMO ^e /eV
[PtL ³ Cl] ^f	335 (5710), 381 (6900), 412 (6780), 460 (190), 495 (130)	505, 539, 578	0.68	7.8	3.3	16	−2.27 ^g	0.36 ^g	−5.10 ^g	−2.53 ^g
[PtL ⁶ Cl] ^f	332 (5640), 363 (3850), 381 (5410), 410 (5210), 492sh (130)	501, 534, 574sh	0.62	7.9	1.0	7.4	−2.30	0.70	−5.58	−2.50
[PtL ³ C≡CC ₆ H ₃ F ₂]	335sh (4928), 388 (5092), 406 (4529), 493 (111)	508, 538, 580sh	0.77	7.8	2.9	15	−2.27	0.25	−4.95	−2.53
[PtL ⁶ C≡CC ₆ H ₃ F ₂]	333 (7395), 366 (7971), 387 (7174), 405 (5814), 489 (290)	500, 529, 572sh	0.66	5.9	0.5	15	−2.28	0.50	−5.30	−2.52

^a Luminescence quantum yield in degassed solution. ^b τ_0 is the lifetime at infinite dilution and k_Q^{SQ} the self-quenching rate constant, determined from the intercept and slope, respectively, of a plot of the measured emission decay rate constant against concentration. ^c Bimolecular rate constant for quenching by molecular oxygen, estimated using the lifetimes in degassed and air-equilibrated solutions, and taking $[\text{O}_2] = 2.2 \times 10^{-3} \text{M}$ in CH₂Cl₂ at 1 atm pressure of air. ^d All processes were electrochemically irreversible, hence E_p^{ox} and E_p^{red} refer to peak potentials of oxidation and reduction, respectively; values are reported relative to a ferrocenium–ferrocene (Fc^+/Fc) redox couple used as an internal reference ($E_{1/2} = +0.42 \text{V}$ vs. saturated calomel electrode SCE); at 298 K, in the presence of 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte, scan rate 200mV s^{-1} . ^e Energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as calculated from the redox potentials. ^f Data from ref. 17 and 21. ^g Data from ref. 31.

**Fig. 1** Absorption spectra of the two acetylide complexes (solid lines) and of the chloro complexes (dotted lines) in CH₂Cl₂ at 298 K.**Fig. 2** Photoluminescence spectra of $[\text{PtL}^3\text{-C}\equiv\text{CC}_6\text{H}_3\text{F}_2]$ in CH₂Cl₂ at 298 K over a 12-fold concentration range, normalized to the monomer emission maximum ($1.75 \times 10^{-5} \text{M}$, black; $2.3 \times 10^{-5} \text{M}$, blue; $6.9 \times 10^{-5} \text{M}$, green; $2.1 \times 10^{-4} \text{M}$, red). The proportion of excimer emission increases with increasing concentration.

than their L³ counterparts (factor of 3 and 6 for the chloride and acetylide complexes respectively), which can reasonably be attributed to the steric hindrance associated with the mesityl group disfavoured approach of molecules to one another.

OLED configurations

Complexes $[\text{PtL}^3\text{-C}\equiv\text{CC}_6\text{H}_3\text{F}_2]$ and $[\text{PtL}^6\text{-C}\equiv\text{CC}_6\text{H}_3\text{F}_2]$ were examined as phosphors for OLEDs, both as dopants at low concentration in a blend with a host material, and as pure films, where the intermolecular interactions might be expected to become important. OLEDs were fabricated by growing a sequence of thin layers on glass substrates pre-coated with indium tin oxide (ITO), transparent to the light generated in the emitting layer (EML). Holes were injected from the ITO anode, and passed through a 60 nm thick hole-transporting layer comprised of a blend of TPD $\{N,N'$ -diphenyl- N,N' -bis(3-methyl)-1,1'-biphenyl-4,4'-diamine, 75%} and PC $\{\text{bisphenolol-A-polycarbonate, 25}\%$ and a 10 nm thick layer of TCTA $\{4,4',4''\text{-tris}(N\text{-carbazolyl})\text{triphenylamine}\}$. They recombine in the EML (30 nm thick, comprised either of 5% Pt complex in TCTA or of the pure complex) with electrons injected from an Al/LiF cathode and transported through a 30 nm layer of TAZ (for details of the materials and experimental procedure, see ref. 32).

Fig. 3 shows the electroluminescence (EL) spectra of OLEDs prepared using $[\text{PtL}^3\text{-C}\equiv\text{CC}_6\text{H}_3\text{F}_2]$ or $[\text{PtL}^6\text{-C}\equiv\text{CC}_6\text{H}_3\text{F}_2]$, in each case using an EML comprising either 5 wt% of the complex in TCTA or the neat complex. The EL spectra of the OLEDs with 5 wt% of the complex in TCTA are quite similar to one another and are clearly characterized by emission from the monomolecular excited states. There is simply a very small blue shift upon substitution of the methyl group by the mesityl, mirroring the behaviour observed in solution. The electroluminescence spectra of OLEDs based on the neat complexes as the EML, on the other hand, exhibit lower-energy, structureless, excimer-like emissions, with λ_{max} of 672 nm and 685 nm, similar to observations on devices employing $[\text{PtL}^3\text{Cl}]$ or $[\text{PtL}^6\text{Cl}]$.^{33,34}

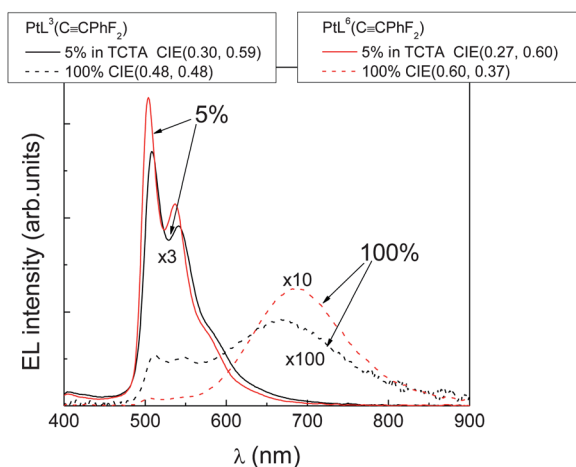


Fig. 3 Electroluminescence spectra of OLEDs based on $[\text{PtL}^3\text{-C}\equiv\text{C-PhF}_2]$ (black colour) or $[\text{PtL}^6\text{-C}\equiv\text{C-PhF}_2]$ (red colour), either as a dopant at 5 wt% in TCTA, or as the neat emitting layer.

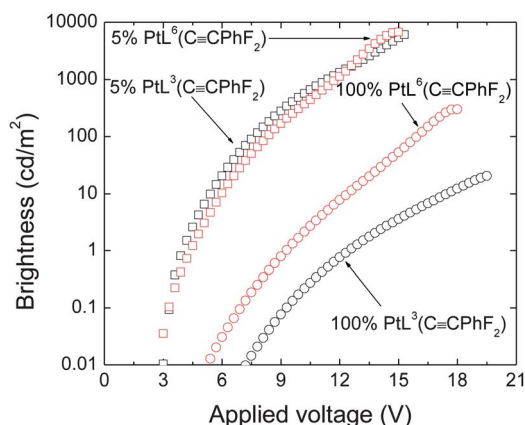


Fig. 4 Brightness versus applied voltage of the OLEDs.

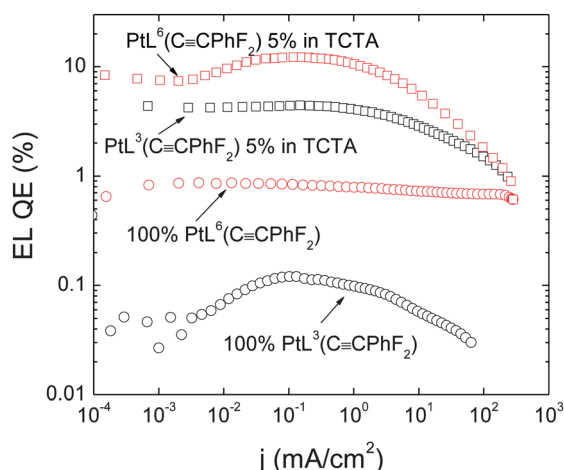


Fig. 5 External quantum efficiencies versus electric current density for the four OLEDs.

Fig. 4 shows the brightness versus voltage plot for the four different OLEDs, whilst Fig. 5 shows the electroluminescence quantum efficiencies (EL QE) versus the electric current density.

As is evident from Fig. 4, the OLEDs with an EML containing 5% platinum complex in TCTA have a similar brightness to one another (reaching up to 7000 cd m^{-2} at high voltage). The electroluminescence quantum efficiency (QE) of the OLED with 5% $[\text{PtL}^3\text{-C}\equiv\text{C-C}_6\text{H}_3\text{F}_2]$ in TCTA is high ($\text{QE}_{\text{max}} \approx 5\%$), similar to that displayed by the device based on the parent chloride complex (*ca.* 8%).³³ On the other hand, the corresponding device comprising $[\text{PtL}^6\text{-C}\equiv\text{C-C}_6\text{H}_3\text{F}_2]$ displays $\text{QE}_{\text{max}} \approx 12\%$. This value is about three times higher than that of a similarly constructed OLED with $[\text{PtL}^6\text{Cl}]$,³³ and more than an order of magnitude superior to OLEDs based on related C^NN^N coordinated platinum complexes of 6-aryl-2,2'-bipyridines with phenylacetylide coligands, for which the EL QE decreases from 1.6% to 0.9% on going from a 2% to a 4% Pt-doped device.¹⁴ The superiority of $[\text{PtL}^6\text{-C}\equiv\text{C-C}_6\text{H}_3\text{F}_2]$ over $[\text{PtL}^3\text{-C}\equiv\text{C-C}_6\text{H}_3\text{F}_2]$, despite the similarity of their solution photophysical and electrochemical properties, is likely to be due to inhibition of "aggregate-induced quenching", owing to the steric bulk of the mesityl group.

Interestingly, however, a similar trend emerges in the devices comprising neat complexes as the EML. The device made from $[\text{PtL}^6\text{-C}\equiv\text{C-C}_6\text{H}_3\text{F}_2]$ displays quantum efficiencies over an order of magnitude superior to those obtained using $[\text{PtL}^3\text{-C}\equiv\text{C-C}_6\text{H}_3\text{F}_2]$ (Fig. 5), much less pronounced roll-off of QE with increasing current, and substantially higher brightness for a given applied voltage (Fig. 4). Clearly, bimolecular interactions must be occurring in this system too, in order to give rise to the low-energy band which is characteristic of an excimer/aggregate species, yet they do not compromise the performance as they do in the complex with the L^3 ligand. A possible explanation is that the presence of the mesityl group favours a head-to-tail arrangement of molecules, as observed in the crystal structure of a related biphenyl-substituted complex for example,²¹ whilst a head-to-head arrangement is possible for the methyl-substituted complex (*e.g.* as also found in the analogue of $[\text{PtL}^3\text{Cl}]$ incorporating a bromine atom in place of the methyl group).³⁵ The results suggest that differing arrangements of the molecules with respect to one another in the EML may be associated with the different formation of emitting or quenching bimolecular aggregations.

Conclusions

In summary, substitution of the chloride ligand of $[\text{PtL}^3\text{Cl}]$ and $[\text{PtL}^6\text{Cl}]$ (L^3 = 5-methyl-1,3-di(2-pyridyl)benzene; L^6 = 5-mesityl-1,3-di(2-pyridyl)benzene) by 3,5-difluorophenyl-acetylide leads to novel Pt complexes, characterized by an improved luminescence in solution. We have shown that they can be used as phosphors for highly efficient phosphorescent OLEDs. Moreover, the introduction of substituents which hinder the close head-to-head interfacial approach of molecules has been shown to inhibit the self-quenching effect of this class of Pt complexes, which can compromise their use as OLED emitters. Thus, by employing the mesityl group on the central ring of the N^CN^CN ligand, a substantial improvement in device efficiency is observed, with EL QE_{max} reaching a value of $\sim 12\%$ for an EML containing 5% of the complex in TCTA. These results show that the new family of 1,3-di(2-pyridyl)-benzene Pt(II) acetylide complexes may represent a useful and appealing tool for the

preparation of efficient OLEDs, and that further improvements may be anticipated through judicious choice of the co-ligand as well as the terdentate ligand.

Acknowledgements

This work was supported by MIUR (FIRB 2004: RBPR05JH2P and PRIN 2008: 2008FZK5AC_002), by Consorzio MIST E-R (project FESR-Tecnopolo AMBIMAT), and by Italian MISE (project Industria 2015 "ALADIN").

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